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Technical Report No. 123

The Behavior of Microdisk and Microring Electrodes.
The Chronoamperometric Response at Microdisk and Microring Electrodes

by

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Prepared for publication in J. Electroanal. Chem.

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July 15, 1988

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale. Distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 123		7a. NAME OF MONITORING ORGANIZATION	
6a. NAME OF PERFORMING ORGANIZATION University of Utah	6b. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code)	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Henry Eyring Building Salt Lake City, UT 84112		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0470-P0003	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program, Code 1113 800 N. Quincy Street Arlington, VA 22217		PROGRAM ELEMENT NO.	PROJECT NO.
11. TITLE (Include Security Classification) The Behavior of Microdisk and Microring Electrodes. The Chronoamperometric Response at Microdisk and Microring Electrodes		TASK NO.	WORK UNIT ACCESSION NO.
12. PERSONAL AUTHOR(S) L.J. Li, M. Hawkins, J.W. Pons, M. Fleischmann, S. Pons and L.M. Abrantes			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 9/87 TO 7/88	14. DATE OF REPORT (Year, Month, Day) July 15, 1988	15. PAGE COUNT 4
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	microelectrodes , mass transport	
	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Attached.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Stanley Pons		22b. TELEPHONE (Include Area Code) (801)581-4760	22c. OFFICE

Abstract

We report the theoretical chronoamperometric response for a ring electrode of finite size, and compare the experimental response to that of a disk electrode. As expected, the response of the ring electrode approaches mass transport conditions close to those for the final steady state at times which are short compared to those at which the steady state is reached for disks of similar radii. The theoretical analysis is based on the properties of discontinuous integrals of Bessel functions which give exact solutions to diffusion problems with discontinuous boundary conditions in the circular cylindrical coordinate system.



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THE BEHAVIOR OF MICRODISK AND MICRORING ELECTRODES.
THE CHRONOAMPEROMETRIC RESPONSE AT MICRODISK AND
MICRORING ELECTRODES.

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Introduction

We have previously derived the exact response for chronoamperometric experiments at disk microelectrodes (1,2) under conditions of uniform surface flux. We have discussed (3) the significance of this approximation and its implications. Additionally, we have discussed (4) the advantages in using ring microelectrodes; the significant increase of mass transport rates to ring geometries compared to disks leads to greater convenience in the measurement of kinetic parameters.

While the problem of the mixed boundary conditions governing electron transfer reactions and the mass transfer process at electrodes of finite size has presented many difficulties for the solution of the diffusion equation, workers have reported a number of approximate solutions and numerical simulations to the problem (5-11). While most of these assume a uniform surface concentration model, a uniform surface flux model is probably more appropriate; the true solution will lie between these limiting cases. Additionally, we have shown that there is only a small difference in these solutions; the greatest errors will occur when assuming uniform flux conditions when the limiting current has been reached, or when assuming uniform concentration conditions early in the experiment when the reaction is kinetically controlled (1). The complete response, which must treat the transition from pure kinetic control to total mass transport control has been determined by applying Neumann's integral theorem and will be the subject of other reports (12-16). We present here the analysis of the problem at a ring and a disk based on the use of discontinuous Bessel integrals. The result is an expression (given in Laplace space) for the response that can be inverted at all times; this has been a difficulty in other work (5,10-11). The expressions give the known limiting cases at short and long times.

At very small microelectrodes, chronoamperometric experiments will not be

particularly useful because of the rapid approach to a steady state and the difficulties in measuring fast transients at low current levels. However, there are numerous special applications (1) where the technique may be interesting.

Experimental

All solutions were prepared from water from a Nanopure (Barnstead) system; chemicals were all analytical reagent grade and were used as received. The solutions used were 1, 5, and 10mM $\text{Ru(III)(NH}_3)_6^{3+}$ in 0.1M KCl and 1mM Fe(II)(CN)_6^{4-} in 0.1M KNO_3 . The solutions were thoroughly purged with nitrogen before making measurements. The secondary - pseudo reference electrode was a large platinum wire. The working electrodes were 1, 5, 10, and 25 μm diameter platinum disk electrodes (from the appropriate wires obtained from Goodfellow Metals), and a gold ring electrode with a diameter of 2.4 μm and a thickness of approximately 300 \AA (*vide infra*). These were made as described previously (4).

The potential step was applied by a wave form generator (Hi-Tek Instruments model PPR1), and the current response was measured by a fast current amplifier (Keithley model 427). Under the conditions of these experiments, the rise time of the amplifier was faster than 60 μs . The transients were recorded on a 125MHz Lecroy model 9400 digitizing oscilloscope. We made all measurements inside an aluminum Faraday cage to reduce capacitatively coupled noise; all leads were kept as short as possible and connections to the cell were made through bulkhead connectors using low noise coaxial cable.

Keywords: Cations, Rubidium compounds, Iron, Cations, Cations, Anions, Electrochemistry

Theoretical Considerations, Results, and Discussion

In the previous work on chronoamperometry at the disk (2), we investigated the general solution to the diffusion equation in circular cylindrical coordinates

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2} + \frac{D}{r} \frac{\partial C}{\partial r} + D \frac{\partial^2 C}{\partial z^2} \quad [1]$$

under conditions of constant, uniform surface flux across the surface of the disk

$$D \left[\frac{\partial C}{\partial z} \right] = Q \quad 0 < r < a, z = 0 \quad [2]$$

which is

$$C = C^\infty - \frac{Qa}{D} \int_0^\infty \exp[-\lambda z] J_0(\lambda r) J_1(\lambda a) \frac{d\lambda}{\lambda} \quad [3]$$

We showed in that work that the general result for the surface concentration in the non-steady state due to a surface flux $Q(t)$ is given in Laplace space by

$$\bar{C} = \frac{C^\infty}{s} - \frac{Q(s)a}{D} \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \quad [4]$$

Here we have $q^2 = \frac{s}{D}$. The average surface concentration is

$$\begin{aligned} \bar{C}_{Av} &= \frac{C^\infty}{s} - \frac{Q(s)a}{D} \int_0^a \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{r \, d\alpha \, dr}{(\alpha^2 + q^2)^{1/2}} \\ &= \frac{C^\infty}{s} - \frac{2Q(s)}{D} \int_0^\infty \left[J_1(\alpha a) \right]^2 \frac{d\alpha}{\alpha(\alpha^2 + q^2)^{1/2}} \end{aligned} \quad [5]$$

from which we derived the flux

$$\begin{aligned} Q(s) &= \frac{\frac{(C^\infty - C_{Av})a}{2} \frac{D^{1/2}}{as^{1/2}}}{\int_0^\infty \left[J_1\left(\beta \frac{as^{1/2}}{D^{1/2}}\right) \right]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}}} \\ &= \frac{(C^\infty - C_{Av})a}{2} \Phi_2 \left(\frac{as^{1/2}}{D^{1/2}} \right) \end{aligned} \quad [6]$$

where we have defined the variable

$$\beta = \frac{D^{1/2} \alpha}{s^{1/2}} \quad [7]$$

We have tabulated the function $\Phi_2(2)$ as a function of the dimensionless parameter $as^{1/2}/D^{1/2}$. The function is readily evaluated by most numerical integration techniques that handle oscillatory integrands; excellent accuracy

is obtained using a modified Burlirsch-Stoer method (17).

Equation [6] when inverted at low values of s (long t) gives the known steady state result (4)

$$Q = \frac{3\pi D}{8a} (C^\infty - C_{Av}) \quad [8]$$

whereas at large values of s (short t) we obtain the expected Cottrell behavior

$$Q = \frac{D^{1/2} (C^\infty - C_{Av})}{\pi^{1/2} t^{1/2}} \quad [9]$$

At other values of $as^{1/2}/D^{1/2}$ the values of $\Phi_2(as^{1/2}/D^{1/2})$ can be represented (maximum deviation 0.4%) by the rational function representation

$$\frac{2Q(s)}{(C^\infty - C_{Av})a} \cong \frac{1.3001 D^{1/2}}{as^{1/2}} + \frac{3\pi D}{4a^2 s} + \frac{0.6999 D^{1/2}/a}{1.79184 D^{1/2}/a + s^{1/2}} \quad [10]$$

Inversion then gives the flux

$$Q(t) \cong \frac{D(C^\infty - C_{Av})}{2a} \cdot \left\{ \frac{3\pi}{4} + \frac{1.3001}{\pi^{1/2}} \left(\frac{a^2}{Dt} \right)^{1/2} + \frac{0.6999}{\pi^{1/2}} \left(\frac{a^2}{Dt} \right)^{1/2} \right. \\ \left. - (0.6999)(1.79184) \exp \left[1.79184 \cdot \frac{D^{1/2} t^{1/2}}{a} \right]^2 \cdot \operatorname{erfc} \left[1.79184 \cdot \frac{D^{1/2} t^{1/2}}{a} \right] \right\}$$

$$\begin{aligned}
- \frac{(C^\infty - C_{Av})}{2a} \cdot \left\{ \frac{3\pi}{4} + \frac{2.000}{\pi^{1/2}} \left(\frac{a^2}{Dt} \right)^{1/2} - 1.2541 \cdot \right. \\
\left. \cdot \exp \left[1.79184 \cdot \frac{D^{1/2} t^{1/2}}{a} \right]^2 \cdot \operatorname{erfc} \left[1.79184 \cdot \frac{D^{1/2} t^{1/2}}{a} \right] \right\}
\end{aligned}
\tag{11}$$

which gives the correct long and short time limits.

The problem of the ring electrode may be solved similarly. The average concentration distribution over a disk source (the above analysis was based on a disk sink) is given by

$$\begin{aligned}
\bar{C}_{Av} &= \frac{C^\infty}{s} + \frac{Q(s)a}{D} \int_0^a \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{r \, d\alpha \, dr}{(\alpha^2 + q^2)^{1/2}} \\
&= \frac{C^\infty}{s} + \frac{2Q(s)}{D} \int_0^\infty \left[J_1(\alpha a) \right]^2 \frac{d\alpha}{\alpha(\alpha^2 + q^2)^{1/2}}
\end{aligned}
\tag{12}$$

so that if we superimpose a disk sink of strength $Q(s)$ and radius b on the source disk of radius a , the combined source and sink give rise to a ring sink of strength $Q(s)$ and dimension $a < r < b$. Proceeding as above, $Q(s)$ may then be determined from

$$\begin{aligned} \frac{C^\infty - C_{Av}}{s} &= \frac{2Q(s)b}{D(b^2 - a^2)} \int_a^b \int_0^\infty J_0(\alpha r) J_1(\alpha b) \frac{r \, d\alpha \, dr}{(\alpha^2 + q^2)^{1/2}} \\ &\quad - \frac{2Q(s)a}{D(b^2 - a^2)} \int_a^b \int_0^\infty J_0(\alpha r) J_1(\alpha a) \frac{r \, d\alpha \, dr}{(\alpha^2 + q^2)^{1/2}} \end{aligned} \quad [13]$$

which is readily integrated to give

$$\begin{aligned} \frac{C^\infty - C_{Av}}{s} &= \frac{2Q(s)}{D(b^2 - a^2)} \left\{ b \int_0^\infty J_1(\alpha b) \left\{ b J_1(\alpha b) - a J_1(\alpha a) \right\} \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \right. \\ &\quad \left. - \left\{ a \int_0^\infty J_1(\alpha a) \left\{ b J_1(\alpha b) - a J_1(\alpha a) \right\} \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \right. \right. \\ &\quad \left. - \frac{2Q(s)}{D(b^2 - a^2)} \left\{ b^2 \int_0^\infty [J_1(\alpha b)]^2 + a^2 \int_0^\infty [J_1(\alpha a)]^2 \right. \right. \\ &\quad \left. \left. - 2ab \int_0^\infty J_1(\alpha b) J_1(\alpha a) \right\} \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \right\} \end{aligned} \quad [14]$$

Therefore the flux may be written as

$$Q(s) = \frac{D(C^\infty - C_{Av})}{2} \frac{1}{s \left\{ \frac{b^2}{(b^2 - a^2)} \int_0^\infty [J_1(\alpha b)]^2 \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} + \frac{a^2}{(b^2 - a^2)} \int_0^\infty [J_1(\alpha a)]^2 \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} - \frac{2ab}{(b^2 - a^2)} \int_0^\infty J_1(\alpha b) J_1(\alpha a) \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \right\}}$$

[15]

Again we make the substitution

$$\beta = D^{1/2} \alpha / s^{1/2} \quad [16]$$

and additionally

$$\gamma = b / a \quad [17]$$

to obtain

$$Q(s) = \frac{(C^\infty - C_{Av})a}{2} \cdot \frac{D^{1/2}}{as^{1/2}} \frac{1}{\left\{ \frac{\gamma^2}{(\gamma^2 - 1)} \int_0^\infty [J_1\left(\beta \gamma \frac{as^{1/2}}{D^{1/2}}\right)]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}} + \frac{1}{(\gamma^2 - 1)} \int_0^\infty [J_1\left(\beta \frac{as^{1/2}}{D^{1/2}}\right)]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}} - \frac{2\gamma}{(\gamma^2 - 1)} \int_0^\infty J_1\left(\beta \gamma \frac{as^{1/2}}{D^{1/2}}\right) J_1\left(\beta \frac{as^{1/2}}{D^{1/2}}\right) \frac{d\beta}{(\beta^2 + q^2)^{1/2}} \right\}}$$

[18]

which can be written in the more convenient form

$$Q(s) = \frac{(C^{\infty} - C_{Av})a}{2} \Phi_{12} \left(\gamma, \frac{D^{1/2}}{as^{1/2}} \right) \quad [19]$$

We evaluate $Q \left(\gamma, \frac{D^{1/2}}{as^{1/2}} \right)$ in the same way described for the disk. Φ_{12} is again determined from an appropriate integration method.

The behavior of disks and rings is compared in the Laplace plane in Figures 1(a) and (b). Figure 1(a) shows that in the region corresponding to short times, large s , $Q(s)s^{1/2}$ is independent of s , i.e. $Q(s) \propto s^{-1/2}$ so that $Q(t) \propto t^{-1/2}$ for both disk and ring electrodes i.e. the behavior follows the Cottrell equation. The duration of this region is determined by the time range for which the transient is dominated by planar diffusion and this duration therefore decreases with decreasing γ i.e. with decreasing ring thickness. In the region corresponding to long times, small s , $Q(s)s$ becomes independent of s , i.e. $Q(s) \propto s^{-1}$ so that the flux reaches a steady state, Figure 1(b). It can be seen that the magnitude of this steady state flux increases markedly with decreasing ring thickness (1) (decreasing γ). Figure 1(b) also shows that for ring electrodes, this region is preceded by a section where $Q(s)s$ is nearly independent of s , i.e. the flux reaches values which are very close to those corresponding to the final steady state at short times; moreover, these times decrease with decreasing γ . This behavior is due to the expansion of the hemi-toroidal diffusion zones which develop around the ring electrodes at times which are long compared to those for which the system follows planar diffusion but at which the final spherical diffusion field has not yet been established. The flux varies approximately with $(\ln t)^{-1}$ in this region.

The sizes of the platinum disk microelectrodes used in the measurements of the chronoamperometric transients were determined from microscopic investigation of the platinum before and after mounting, and from an analysis of the slope of a plot of the limiting current for ferrocyanide reduction vs. nominal electrode radius of the disk determined from the microscopic measurements. The diffusion coefficient of ferrocyanide was determined to be $6.74 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, in good agreement with the literature value (18). Further, the analysis of voltammetric experiments in 1, 5, and 10mM solutions of $\text{Ru(III)(NH}_3)_6^{+++}$ in 0.1M KCl gave an average value for the diffusion coefficient of $6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Wipf et al. (19) have reported a value for D of $6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in 0.1M sodium trifluoroacetate.

Determination of the dimensions of the ring electrode were made by (a) optical and electron microscopy, and (b) measurement of the limiting current of the ruthenium solution and use of Equations [35], [36], and [37] of reference (1).

Chronoamperometric experiments with the disk electrodes were performed on the 1mM $\text{Ru(III)(NH}_3)_6^{+++}$ solutions. The potential was stepped from 0.0 to -350mV (well into the limiting current plateau). The responses are shown in Figure 2. Included in Figure 2 are theoretical responses determined from Equation [11] using the experimental parameters given above.

The results for the ring experiment, including the results predicted from Equation [19] are also included in Figure 2.

The responses for the smaller electrodes for the two geometries are seen to approach steady state values markedly faster than the larger electrodes, as is expected. As predicted, the currents at ring electrodes approach values close to those corresponding to the steady state at times which are short compared to those for disks of comparable radii. Thus the ring electrode used in this experiment has already reached a current within 0.01nA of the steady

state value at about 40ms, whereas the 1 μ m disk has not reached this level at 160ms.

Acknowledgement

We thank the Office of Naval Research for support of th's work.

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Glossary of Symbols Used

a, b	Radius of disk, cm
C	Concentration, mols cm ⁻³
C [∞]	Bulk concentration, mols cm ⁻³
C _{Av}	Average concentration, mols cm ⁻³
D	Diffusion coefficient, cm ² s ⁻¹
J ₀ , J ₁	Bessel functions
q	Parameter (s/D) ^{1/2}
Q	Flux, mols cm ⁻² s ⁻¹
r	Radial coordinate, cm
s	Laplace transform variable
t	Time, s
z	Coordinate normal to plane of disk, cm
α	Continuous dummy integration variable.
β	Parameter D ^{1/2} α/s ^{1/2}
γ	a/b

$$\Phi_2 = \frac{\frac{D^{1/2}}{as^{1/2}}}{\int_0^\infty \left[J_1 \left(\beta \frac{as^{1/2}}{D^{1/2}} \right) \right]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}}}$$

$$\Phi_{12} = \frac{D^{1/2}}{as^{1/2}} \cdot \frac{1}{\left\{ \frac{\gamma^2}{(\gamma^2 - 1)} \int_0^\infty \left[J_1 \left(\beta \gamma \frac{as^{1/2}}{D^{1/2}} \right) \right]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}} \right.}$$

$$+ \frac{1}{(\gamma^2 - 1)} \int_0^\infty \left[J_1 \left(\beta \frac{as^{1/2}}{D^{1/2}} \right) \right]^2 \frac{d\beta}{\beta(\beta^2 + 1)^{1/2}}$$

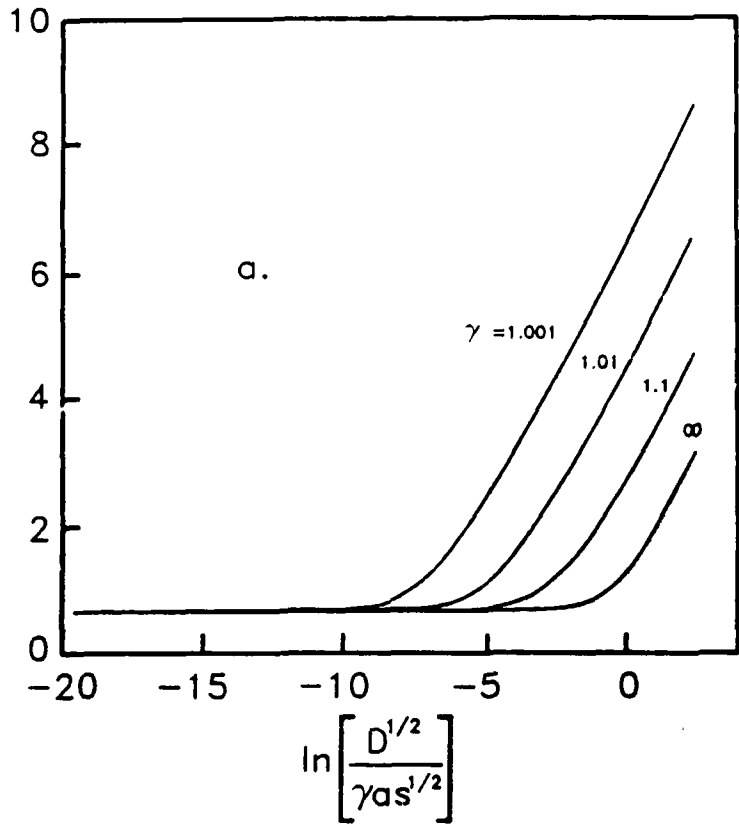
$$\left. - \frac{2\gamma}{(\gamma^2 - 1)} \int_0^\infty J_1 \left(\beta \gamma \frac{as^{1/2}}{D^{1/2}} \right) J_1 \left(\beta \frac{as^{1/2}}{D^{1/2}} \right) \frac{d\alpha}{(\alpha^2 + q^2)^{1/2}} \right\}}$$

Figure Legend

1. Comparison of the behavior of disk and ring electrodes.
 - (a) The behavior of $2Q(s)/(C^\infty - C_{Av})\gamma a \cdot (\gamma a s^{1/2}/D^{1/2})$
 - (b) The behavior of $2Q(s)/(C^\infty - C_{Av})\gamma a \cdot (\gamma a s^{1/2}/D^{1/2})^2$

2. Chronoamperometric responses (circles) and theoretical prediction (solid lines) for Pt disks of various diameters and a ring electrode in 0.1M $\text{Ru(III)(NH}_3)_6^{+++}$ in 0.1M KCl. Potential step was from 0.0 to -350mV vs. Pt pseudo reference.

$$\ln \left[\frac{2Q(s)}{(C^\infty - C_{Av})\gamma a} \cdot \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right) \right]$$



$$\ln \left[\frac{2Q(s)}{(C^\infty - C_{Av})\gamma a} \cdot \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right)^2 \right]$$

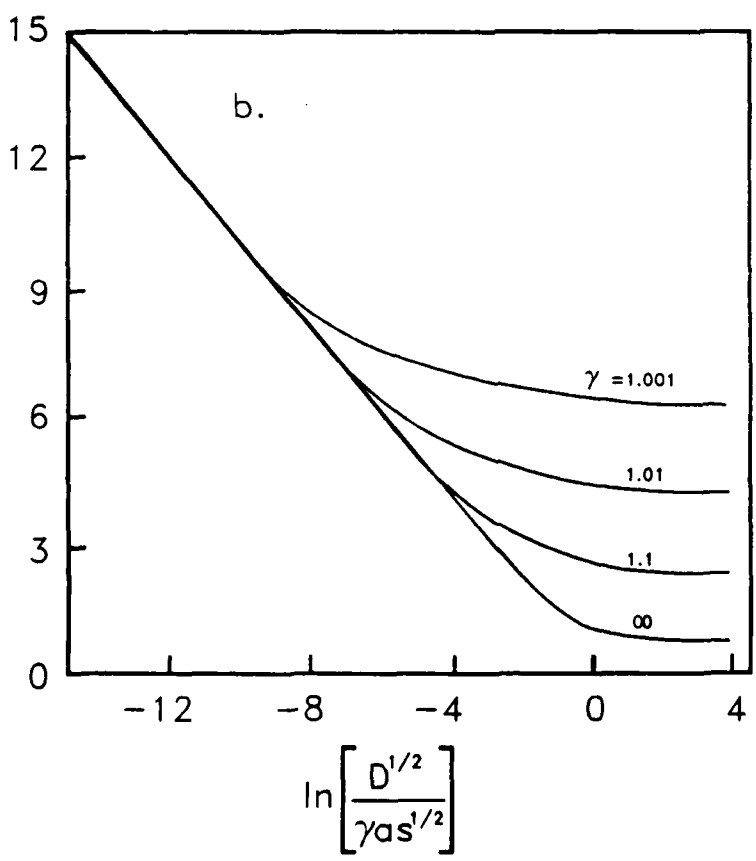


Fig 1

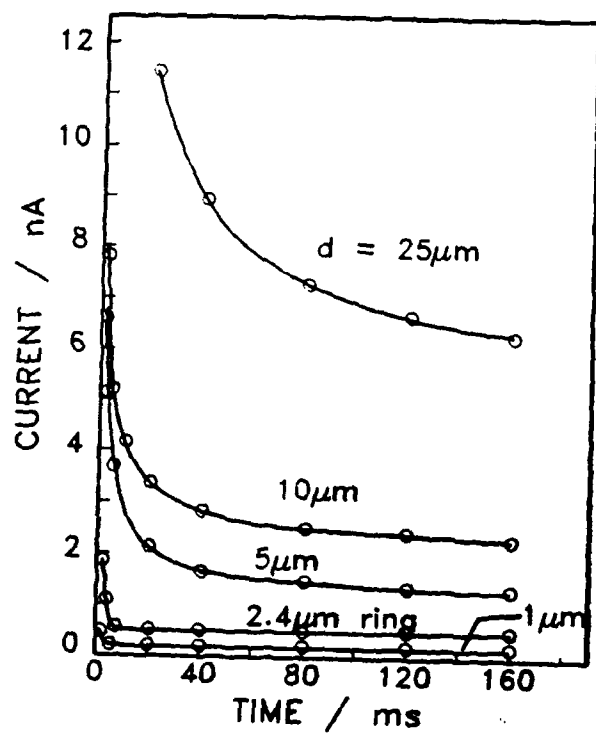
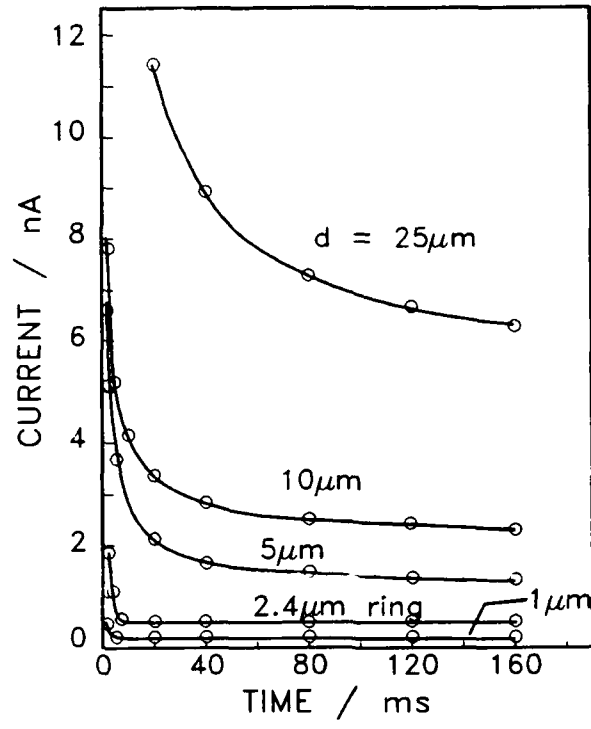
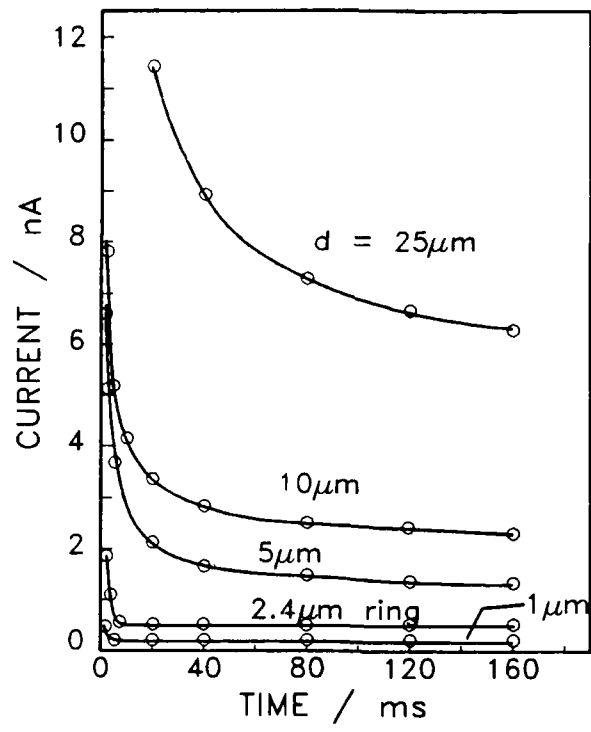
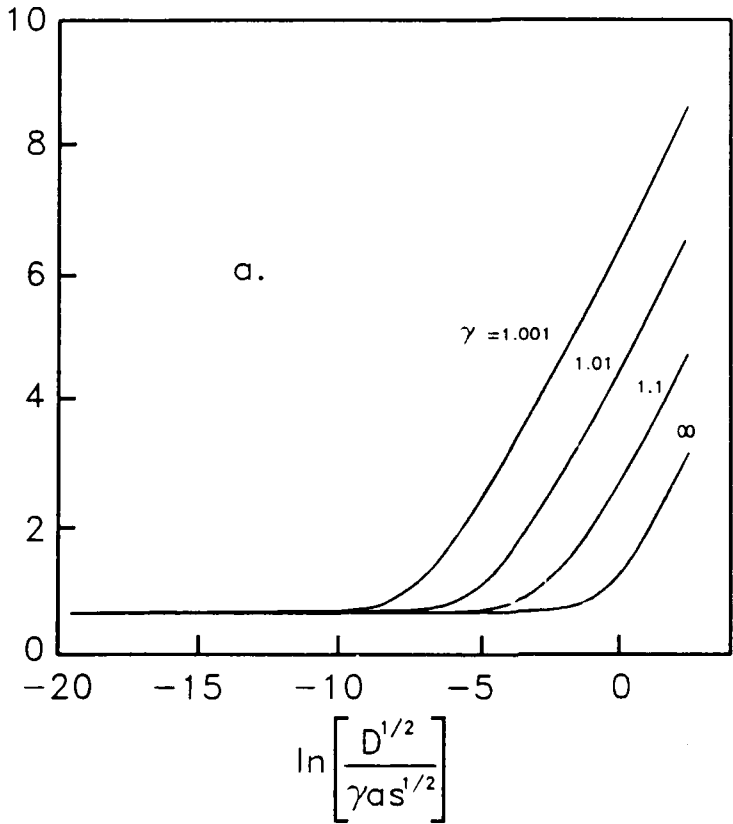


Fig 2

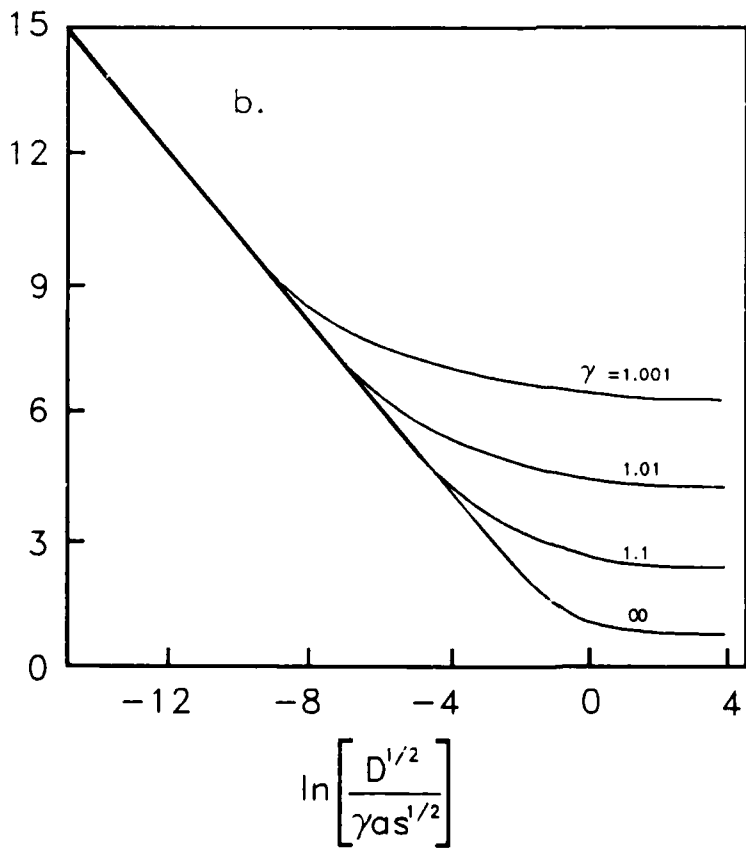




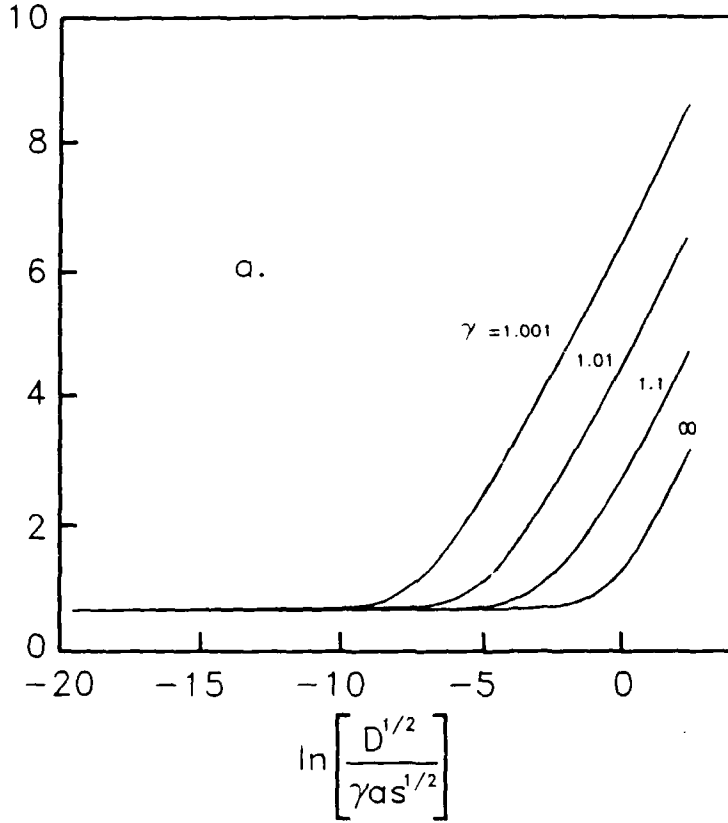
$$\left[\frac{2Q(s)}{\ln \left(\frac{C^\infty - C_{Av}}{C^\infty - C} \right) \gamma a} \right] \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right)$$



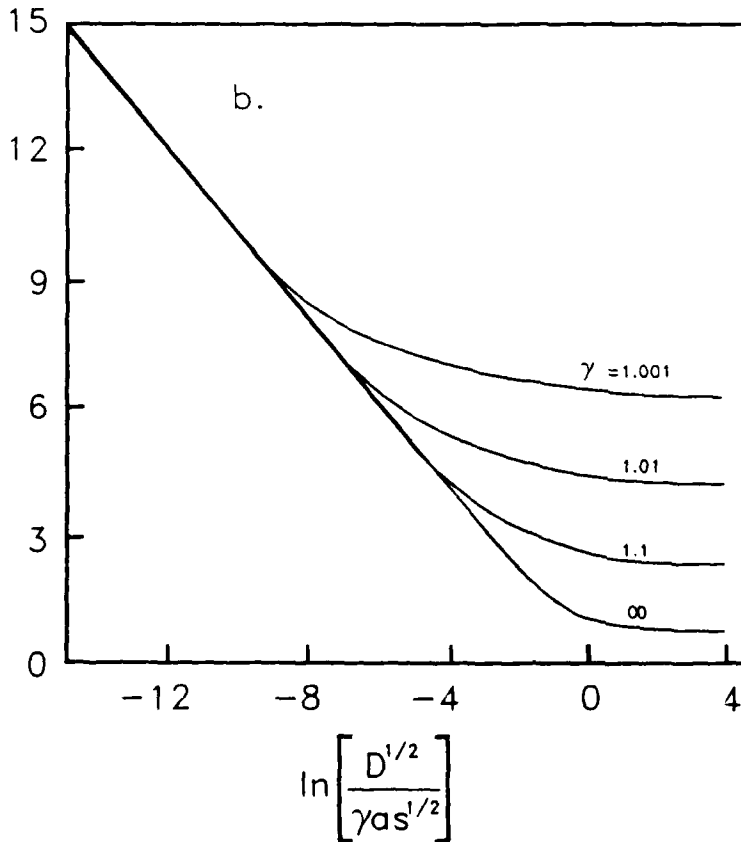
$$\left[\frac{2Q(s)}{\ln \left(\frac{C^\infty - C_{Av}}{C^\infty - C} \right) \gamma a} \right]^2 \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right)$$



$$\ln \left[\frac{2Q(s)}{(C^\infty - C_{Av})\gamma a} \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right) \right]$$



$$\ln \left[\frac{2Q(s)}{(C^\infty - C_{Av})\gamma a} \left(\frac{\gamma a s^{1/2}}{D^{1/2}} \right)^2 \right]$$



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